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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## Phosha-Meerwein Reaction of Diazo Esters

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## PHOSHA-MEERWEIN REACTION OF DIAZO ESTERS

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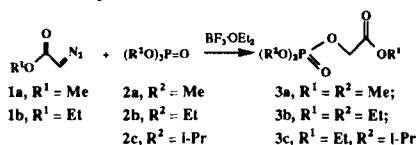
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### Abstract.

Diazo esters (**1a,b**) react with trialkyl phosphates (**2a-c**) in the presence of  $\text{BF}_3 \cdot \text{OEt}_2$  to give the corresponding phosphates (**3a-c**) in 42-58 % yields. The competed intra/intermolecular protonation in the reaction of **1a** with dimethyl hydrogen phosphite leads to phosphonate **4** and phosphite **5**.

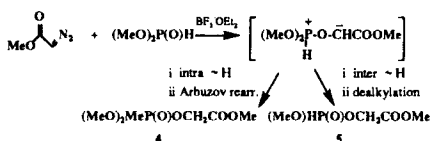
**Key Words:** Diazo ester; dimethyl hydrogen phosphite; Lewis acid catalysis; phoshate; zwitterionic phosphonium intermediate.

We have found that diazo esters (**1a,b**) react with trialkyl phosphates (**2a-c**) in the presence of  $\text{BF}_3 \cdot \text{OEt}_2$  (10 Mol %) to give the corresponding phosphates (**3a-c**) in 42-58 % yields.



The catalytic capability of a set of catalysts indicates a Lewis acid promoted process:  $\text{BF}_3 \cdot \text{OEt}_2$  (52 %) >  $(\text{p-Br-C}_6\text{H}_4)_3\text{N}^+\text{SbCl}_6^-$  (35 %) >  $\text{SnCl}_2$  (17 %) >  $\text{Rh}_2(\text{OAc})_4$  (14 %) >

$\text{Cu}(\text{OTf})_2$  (5 %) (**3a**). Using  $\text{CD}_2\text{Cl}_2$ ,  $\text{D}_2\text{O}$ ,  $(\text{CD}_3\text{O})_3\text{PO}$  and  $\text{N}_2\text{CDCOOCH}_3$ , the reaction is explained by a step mechanism *via* zwitterionic phosphonium intermediate, followed by protonation at C atom by  $\text{H}_2\text{O}$  impurities and dealkylation at P atoms.



The competed intra/intermolecular protonation in the reaction of **1a** with dimethyl hydrogen phosphite leads to mixtute of phosphonate **4** and phosphite **5**, whereas in the presence of

large excess of **1a** a product of complete replacement,  $(\text{MeOOCH}_2\text{O})_2\text{P(O)Me}$  has been isolated, arose from both **4** and **5**.